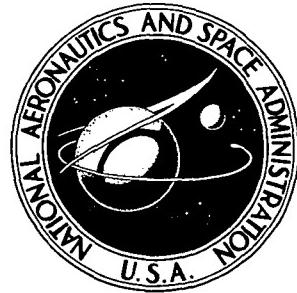


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STRUCTURE AND FUNCTION OF  
AN INORGANIC-ORGANIC SEPARATOR  
FOR ELECTROCHEMICAL CELLS -  
PRELIMINARY STUDY

by John M. Bozek

Lewis Research Center  
Cleveland, Ohio 44135



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JULY 1974

1. Report No. <b>NASA TM X-3080</b>	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle <b>STRUCTURE AND FUNCTION OF AN INORGANIC-ORGANIC SEPARATOR FOR ELECTROCHEMICAL CELLS - PRELIMINARY STUDY</b>		5. Report Date <b>JULY 1974</b>	
7. Author(s) <b>John M. Bozek</b>		6. Performing Organization Code	
9. Performing Organization Name and Address <b>Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135</b>		8. Performing Organization Report No. <b>E-7871</b>	
12. Sponsoring Agency Name and Address <b>National Aeronautics and Space Administration Washington, D.C. 20546</b>		10. Work Unit No. <b>502-25</b>	
		11. Contract or Grant No.	
		13. Type of Report and Period Covered <b>Technical Memorandum</b>	
		14. Sponsoring Agency Code	
15. Supplementary Notes			
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17. Key Words (Suggested by Author(s)) <b>Separators Silver-zinc electrolytic cells Alkaline batteries</b>		18. Distribution Statement <b>Unclassified - unlimited Category 03</b>	
19. Security Classif. (of this report) <b>Unclassified</b>	20. Security Classif. (of this page) <b>Unclassified</b>	21. No. of Pages <b>15</b>	22. Price* <b>\$3.00</b>

\* For sale by the National Technical Information Service, Springfield, Virginia 22151

# STRUCTURE AND FUNCTION OF AN INORGANIC-ORGANIC SEPARATOR FOR ELECTROCHEMICAL CELLS - PRELIMINARY STUDY

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## SUMMARY

The structure of a new separator material for electrochemical cells, U.S. Patent No. 3,625,770, has been investigated. This inorganic-organic separator was originally thought of as consisting of two layers: a substrate and a slurry coating. Investigation into details of the separator structure showed it to be multilayered and to consist mainly of a quasi-impervious organic skin, a porous region of mixed organic and inorganic material, and an area of nonuniformly treated substrate. The essential feature of the coating (slurry) is believed to be interconnected pores which allow ionic conductivity. The interconnected pores are believed to be formed by the interaction of the plasticizer and inorganic fibers.

The major failure mode of silver-zinc cells using such a separator (zinc nodules shorting adjacent plates) was investigated.

## INTRODUCTION

Separators used in silver-zinc (Ag-Zn) cells are generally composed of organic material, usually some form of cellulose or cross-linked grafted polymer. These types of separators perform satisfactorily for about 18 to 24 months of wet life. Failures of Ag-Zn cells using organic separators are usually attributable to silver penetration or zinc dendrite shorting or both due to separator deterioration. Both of these modes of failure are catastrophic in nature. The other main cause of Ag-Zn cell failure, not necessarily due to separator failure, is Zn electrode redistribution (shape change) and concomitant gradual loss of capacity.

These failure modes are generally accepted as typical of organic separators. Moreover, high temperatures accelerate the rates of these types of failures. In an effort to reduce occurrences of these failures, especially where heat sterilization is

required, a new type of separator was developed (U.S. Patent No. 3,625,770, ref. 1). This separator contains not only organic materials but also inorganic materials. Even after heat sterilization at 135° C for 200 hours, the wet life of Ag-Zn cells using this inorganic-organic separator has been extended well beyond the 2 years recognized as the limit for standard Ag-Zn cells with organic separators. Silver-zinc cells using this inorganic-organic separator are still operating after 4 years.

Separator composition and manufacturing techniques are as follows:

- (1) Fuel-cell grade asbestos board (the substrate) is impregnated with a 2 to 10 percent polyphenylene oxide (PPO) - chloroform solution.
- (2) The impregnated asbestos boards are cut and flued into bags to accept electrodes.
- (3) The bags are dipped into a slurry containing
  - (a) PPO and a plasticizer (2 to 48 percent)
  - (b) Ceramic filler (50 to 95 percent)
  - (c) Inorganic fillers (2 to 35 percent)

The resulting dried slurry coat is nominally 0.13 millimeter (5 mils) thick.

The purpose of this investigation is to identify the structure and to obtain data which will aid in determining the operating mechanism of the inorganic-organic separator. Because this inorganic-organic separator was developed empirically, little was known of the structure and mechanism by which the separator functioned. The work described in this report is the initial effort to determine the structure and offer data that may help in clarifying the operating mechanism of the inorganic-organic separator. Such determinations should ultimately aid in defining causes of failure of the separator and possible areas of improvement to further enhance the performance capabilities of electrolytic cells using the inorganic-organic separator.

The approach is to investigate and characterize the completed separator and then to investigate the properties of its component parts. The section Mode of Silver-Zinc Cell Failure deals with the failure mode prevalent in Ag-Zn cells using this separator.

#### EXPERIMENTAL TECHNIQUES USED

A scanning electron microscope (SEM) was used to determine the microfine structure of the membranes. An X-ray energy dispersion spectrometer (EDS) was used to identify chemical elements in the membranes. The microscopic investigation entailed looking at the surface of membrane samples and inspecting their interiors.

Standard techniques (outlined in ref. 2) were used to characterize the separator and its component parts. The component parts were characterized in the form of thin films cast on glass. The resistivity and absorptivity measurements were made after a 5-day ambient soaking in a solution of potassium hydroxide (KOH) and water ( $H_2O$ ). The resistance measurements were normalized to 18° C by using the correction factor derived

from reference 3. These data helped in determining the structure of the separator and the function of the constituents of both the substrate and the slurry coat.

Finally, the Zn nodules identified as the primary failure mode (ref. 4) were analyzed by using SEM, EDS, and standard metallographic mounting and polishing techniques.

## RESULTS AND DISCUSSION

### Scanning Electron Microscope Photographs and Photomicrographs of Separators

The structure of the separator was initially thought to consist of two phases: a substrate and a coating. This was expected from the manufacturing process outlined in the INTRODUCTION.

However, SEM investigation of the surface of the coating on the asbestos substrate revealed a quasi-impervious surface. Figure 1 shows the surface magnified 3000 times. There is evidence of holes (o.d.,  $\sim 1 \mu\text{m}$ ) through the surface, below which the inorganic fibers and ceramic filler are visible as blurs. The density of holes ranges from  $10^5$  to  $10^6$  holes per square centimeter of separator area.

In order to see whether the observed holes totally penetrate the coating, the sample coating was fractured, and a cross-sectional area was viewed with the SEM. A cross section of a typical fracture is shown in figure 2. As can be seen in this angled view, the surface (upper half of photograph) appears to be composed of only a very thin organic layer or "skin." Below this skin is a very porous region (lower half of photograph) composed of inorganic fibers and ceramic filler held in place by an organic web. The holes viewed in figure 1 penetrate only the thin organic skin. Figure 3 shows another area of the porous region of the coating. The fibers and the ceramic filler, with its fine structure, can be seen together with the organic web that holds the inorganic materials in place.

There is reason to believe that the substrate is not a uniform layer. The separator was noticed to delaminate after soaking in a 45 weight percent KOH solution for a few days. The delamination was approximately in the center of the asbestos substrate. Though delamination was complete, the outer surfaces were intact, and only the center section lost all mechanical integrity. Thus, the possibility exists that in a tightly packed electrolytic cell (such as the Ag-Zn cell) the outer layers of asbestos hold intact the rather highly absorptive center section, which has no mechanical strength of itself.

To investigate this point further asbestos sheets were impregnated with a colored PPO-chloroform solution. After curing, the impregnated asbestos sheets were cross-sectioned and polished for inspection. Three layers were seen. The top and bottom layer were darker in color than the center (50 percent) section. This difference tends to indicate that the solution deposited PPO heavily near the surfaces and less heavily, if

at all, near the center. This apparent fractionation of deposited PPO may explain the weakness of the substrate in the center noted previously.

Furthermore, there have been measurements reported on the apparent penetration of the slurry coat into the asbestos substrate. The penetration has been quoted to be 0.025 to 0.050 millimeter (1 to 2 mils) (ref. 4 and unpublished data obtained from Dr. John Parry of Arthur D. Little, Inc.). To define the penetration further, cross-sectional photomicrographs were taken. As shown in figure 4, if there is penetration, it is purely by organic material since no ceramic filler or inorganic fibers penetrated into the substrate. These inorganic materials remained in the top coating.

As a result of these findings, a structure is proposed for the separator under investigation. A schematic drawing of the proposed structure is presented in figure 5. The skin is a very thin membrane of organic material. Some holes are evident in the skin with an outside diameter of around 1 micrometer and a density of  $10^5$  to  $10^6$  holes per square centimeter of surface area. Below the skin is a very porous region composed of a ceramic filler and inorganic fibers in an organic web. The penetration region is 0.025 to 0.050 millimeter (1 to 2 mils) thick; the penetrant is composed of organic material only. The remainder of the substrate is composed of PPO-impregnated asbestos layers on either side of a center section of raw or very lightly impregnated asbestos. The PPO-impregnated asbestos layer next to the penetration region may or may not exist, depending on how deep the penetration is.

### Conductivity and Absorptivity

In an effort to characterize further the structure and mechanism of the inorganic-organic separator, resistivity and KOH absorptivity measurements were made. The results of this investigation are shown in table I. Three membranes were investigated: the completed separator, the substrate (impregnated asbestos), and the coating (as a film cast on glass). The thickness of each substance is shown together with the measured area resistivity and volume percent absorption of 45 weight percent KOH. The complete separator has a rather high absorptivity, a desirable feature in electrolytic cells, but the value varies considerably from sample to sample. This variation can be attributed mainly to the substrate. The substrate, as mentioned previously, is impregnated with PPO and has a lightly impregnated center section which is capable of absorbing large quantities of KOH. Upon soaking, the substrate center section loses all mechanical integrity, and any handling will cause large variations in the determination of absorptivity.

The cast film itself has appreciable absorptivity. The voids of the type noted in figure 3 may contribute to but not necessarily limit the observed high absorptivity of the full separator.

The sum of the area resistivities of the component parts (substrate and cast film) nearly equals the area resistivity of the complete separator. Each component part contributes to the area resistivity of the complete separator, with the cast film contributing significantly more than the substrate.

To determine which of the constituents in the slurry coat are important and what the function of each is, thin films of slurry (all 0.08 to 0.15 mm (3 to 6 mils) thick) were cast on glass. Seven films were cast, with one or more constituents systematically left out, the properties of the films were measured. The important properties of resistivity and absorptivity (KOH and H<sub>2</sub>O) are listed in table II. The constituents marked 0 were eliminated totally from the slurry. Those marked 1 were present in the amounts specified in the normal separator formulation.

Comparison of absorptivity and resistivity of films A and B in table II shows that the addition of the plasticizer reduces resistance and increases both H<sub>2</sub>O and KOH absorptivity. The same effect of adding plasticizer is noted for films C and D. Comparison of data for films E and F shows that the addition of inorganic fibers substantially reduces resistance and substantially increases KOH absorptivity. Inspection of the data for films D and F indicates that the ceramic filler has much the same effect as the inorganic fibers but to a lesser degree. For completeness film G, a pure PPO film, was analyzed. This film showed essentially infinite resistance and zero absorptivity as expected.

Table II indicates that the plasticizer and a filler of some kind, preferably inorganic fibers over the ceramic filler, are needed for low resistivity and increased absorptivity.

In order to define further the role of the plasticizer and fibers, three films were cast for comparison of microstructure under the SEM (see figs. 6 to 8). Figure 6 is a full cross-sectional view of a fractured film, while figures 7 and 8 are angled views of a fractured film with the surface shown in the top half of the photograph and the interior of the film shown in the bottom half of the photograph. As can be seen in figure 6, a pure PPO cast film (similar to film G in table II) had little if any porosity, which would explain the high resistance and low absorptivity noted in table II. Figure 7 shows a cast film of PPO and plasticizer (similar to film E in table II). Porosity due to cellular structure is evident. The low absorptivity and the high resistivity shown in table II for film E might be explained by a possible lack of continuous paths from pore to pore. Finally, figure 8 shows a cross section of a cast film containing PPO, plasticizer, and inorganic fibers (similar to film F in table II). Here again the porosity is evident, but the cellular structure is much smaller and the fibers appear to form paths or a wick between cellular structures.

The noninterconnected cellular structure shown in figure 7 is certainly undesirable, and therefore changing this structure by interconnecting the pores will be beneficial. Such changes appear to be necessary to obtain acceptable absorptivity and resistance.

## Mode of Silver-Zinc Cell Failure

An understanding of the structure discussed in the previous section may aid in determining the mechanism of failure of Ag-Zn cells constructed by using the inorganic-organic separator.

The main failure mode in question is Zn nodule penetration. Failure analyses of Ag-Zn cells (ref. 4) have shown large Zn nodules penetrating two adjacent separator bags and shorting the adjacent Ag and Zn electrodes.

A cross-sectional photomicrograph of such a nodule is shown in figure 9. For a clearer understanding of figure 9, a schematic drawing is presented in figure 10. The Ag-Zn cell from which the nodule was removed was of a double bag design; that is, each electrode, Ag and Zn, had a separator bag around it. As can be seen from figures 9 and 10, the nodule stuck to the Ag electrode bag and pulled away from the Zn electrode bag. The Ag separator was black, while the Zn separator was blue.

The growth of the Zn nodule can be reasonably reconstructed from details shown in figures 9 and 10. The Zn electrode material expanded into the Zn separator asbestos substrate, as shown by the blue coloration of the asbestos substrate. Further expansion of the Zn electrode was in the form of a small nodule through a single point in the Zn separator slurry coating. The Zn nodule spread laterally into the interstitial area between the Zn and Ag separator bags "searching" for a penetration point (hole in the skin) in the Ag separator slurry coating. After penetrating the Ag separator coating, the Zn nodule spread out (mushroomed) in the Ag separator asbestos substrate until contact was made with the Ag electrode. At this point the Ag-Zn cell failed catastrophically by shorting.

Confirmation that the shorting path (fig. 9) is Zn can be obtained by EDS analysis, as shown in figure 11. Three positions adjacent to, and in, the nodule were analyzed. The first position (1 in fig. 9) is in the Ag separator asbestos substrate. Data in figure 11(a) show Ag present but little Zn. The next position (2) analyzed is in the nodule located in the Ag separator substrate, and figure 11(b) shows much Zn but little Ag present. The last position (3) is in the Zn separator asbestos substrate. As figure 11(c) shows, large amounts of Zn are present.

## SUMMARY OF RESULTS

The inorganic-organic semiflexible separator described in U.S. Patent No. 3,625,770 has a far from simple structure. There are at least five, possibly six, discernible layers, each having a function in separator operation. The substrate of asbestos with its three or four layers supplies the electrolyte absorber qualities. The asbes-

tos is also a base or anchor for the slurry coat, which itself is composed of two layers. The slurry coat has a quasi-impervious skin, which may inhibit zinc nodule formation, and a porous region, which acts as an absorber.

The plasticizer and the inorganic fibers of the slurry coating are necessary for acceptable resistivity and absorptivity.

The major failure mode of the separator is shorting caused by penetration of a zinc nodule into adjacent silver and zinc separator bags.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, April 19, 1974,  
502-25.

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4. Smatko, Joseph S.; Weaver, Robert D.; and Kalhammer, Fritz R.: Inorganic Separator Technology Program. SRI-SCU-1377, Stanford Research Institute (NASA CR-121215), 1973.

TABLE I. - COMPLETE SEPARATOR AND COMPONENT PROPERTIES

Sample	Thickness		Resistivity at 18° C with 45 wt. % KOH, Ω-cm <sup>2</sup>	Absorptivity with 45 wt. % KOH, vol. %
	cm	mils		
Complete separator	40×10 <sup>-3</sup>	15.8	1.5	96
Substrate	25	9.9	.5	85
Cast film	13	5.0	.8	35

TABLE II. - CAST FILM PROPERTIES

Sample film	Constituent <sup>a</sup>				Absorptivity, vol. %		Resistivity at 18° C with 45 wt. % KOH, Ω-cm
	Plasticizer	PPO	Ceramic filler	Inorganic fibers	H <sub>2</sub> O	45 wt. % KOH	
A	1	1	- 1	1	25	35	60
B	0	1	1	1	<5	<10	630
C	0	1	1	0	<5	<10	650
D	1	1	1	0	<15	20	180
E	1	1	0	0	---	<10	>1000
F	1	1	0	1	---	50	40
G	0	1	0	0	---	<10	>1000

<sup>a</sup>Constituent eliminated from slurry, 0; constituent present in amount specified in normal separator formulation, 1.



Figure 1. - SEM photograph of surface of separator (arrows point to holes).

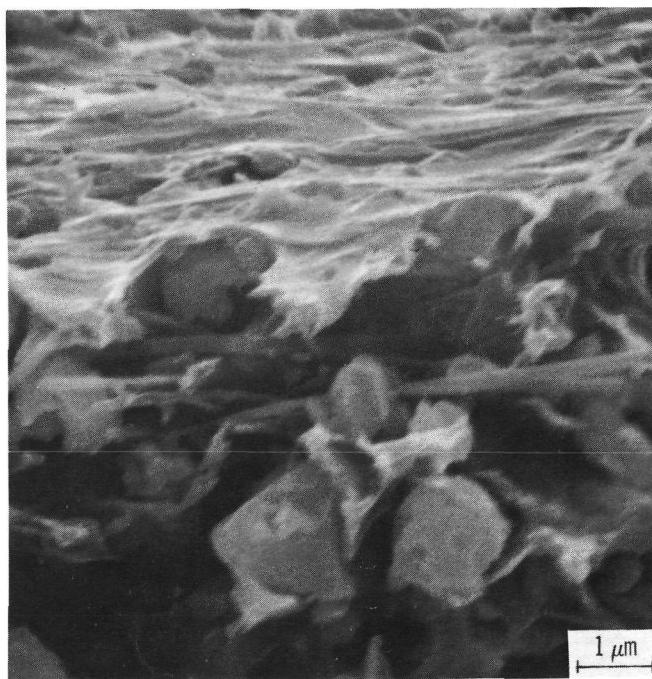


Figure 2. - SEM photograph of fractured complete separator ( $45^\circ$  angle view).



Figure 3. - SEM photograph of center section of coating.

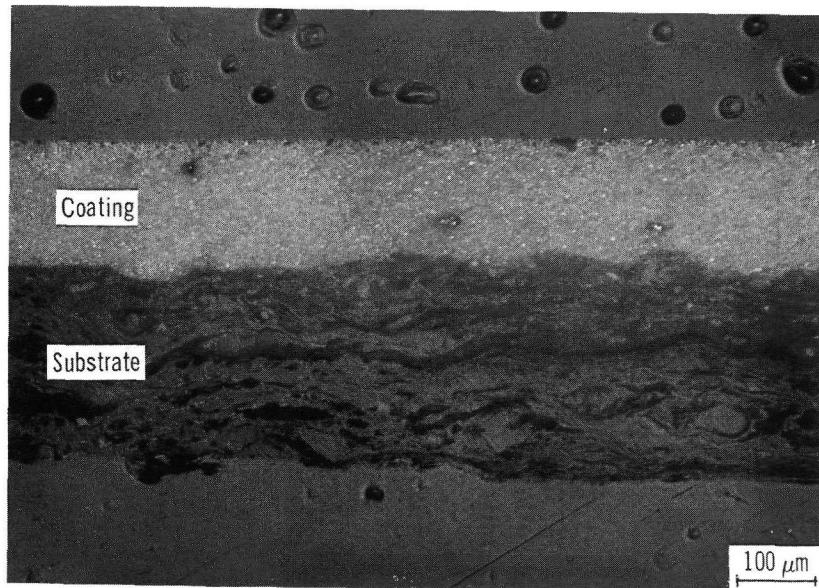


Figure 4. - Photomicrograph of polished cross section of complete separator.

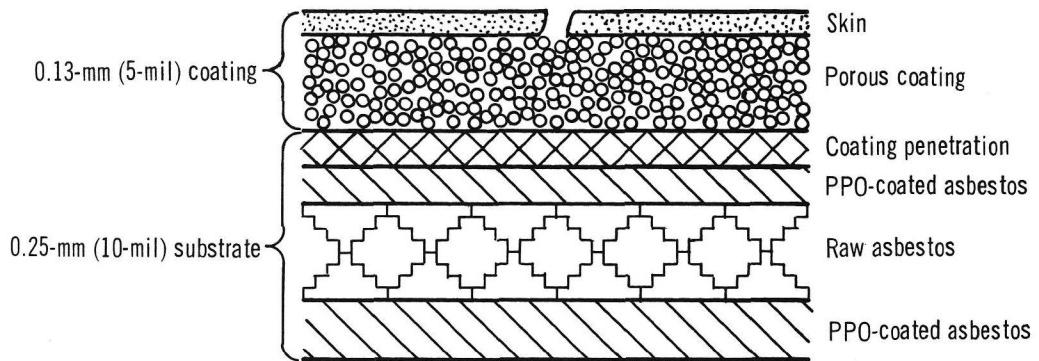


Figure 5. - Present structure concept.

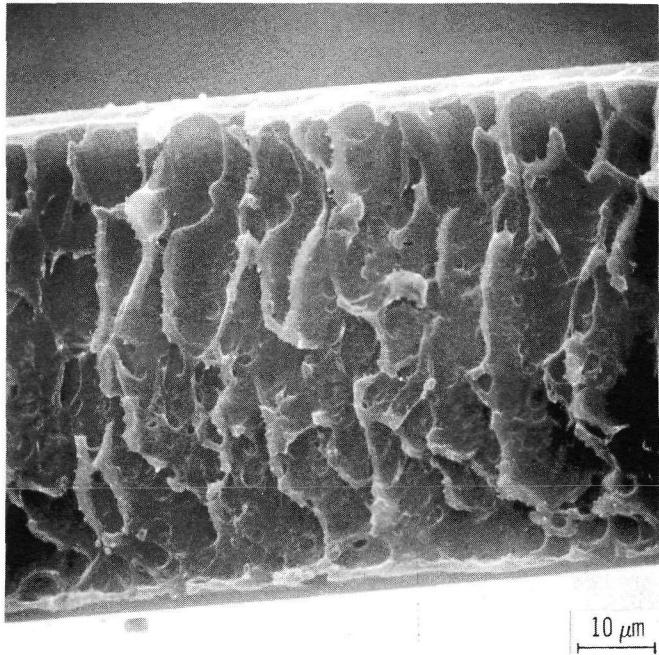


Figure 6. - SEM photograph of cast film of PPO.

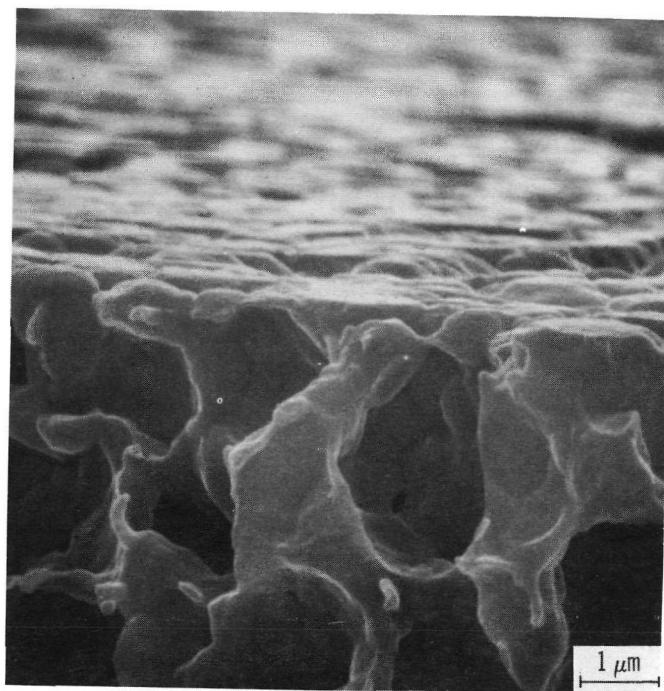


Figure 7. - SEM photograph of cast film of PPO and plasticizer.

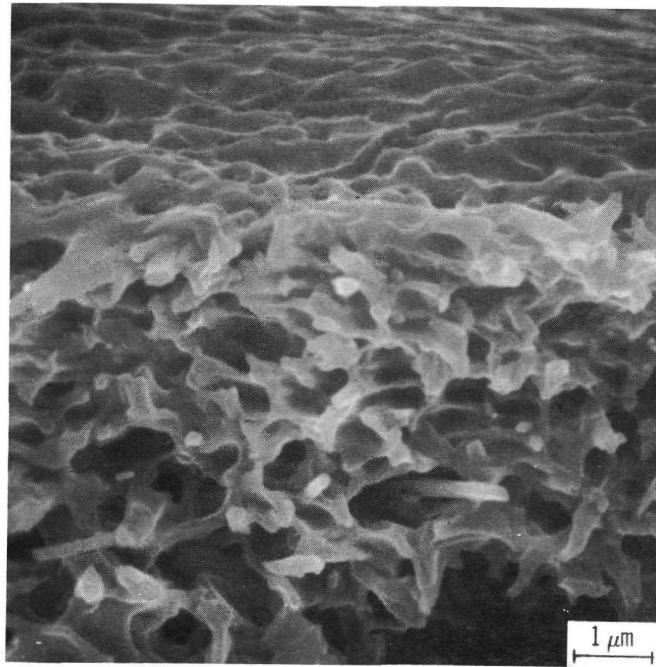


Figure 8. - SEM photograph of cast film of PPO, plasticizer, and inorganic fibers.

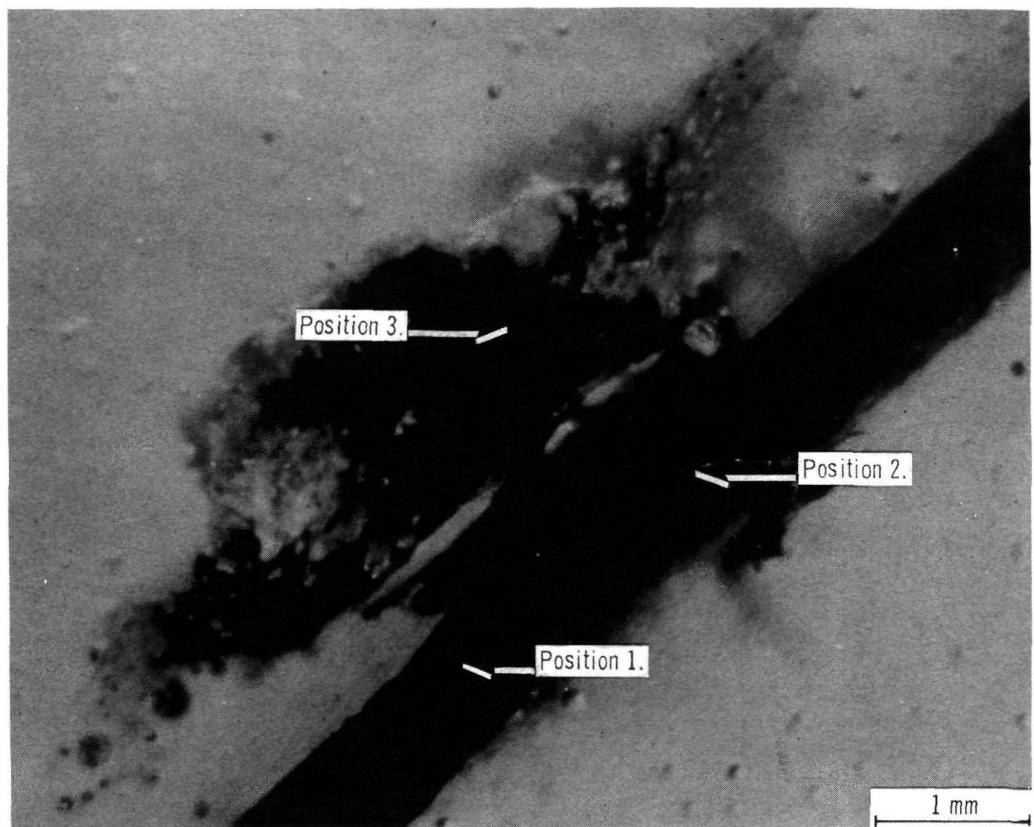


Figure 9. - Polished cross section of zinc failure nodule.

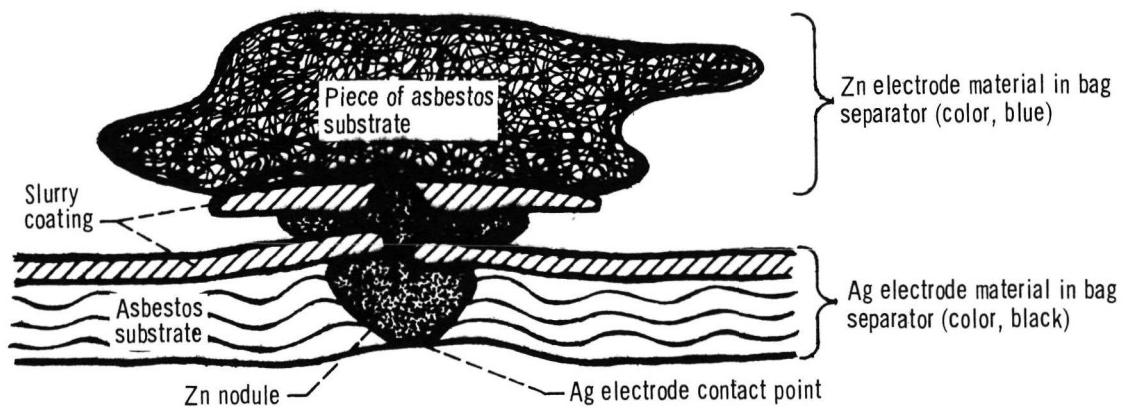
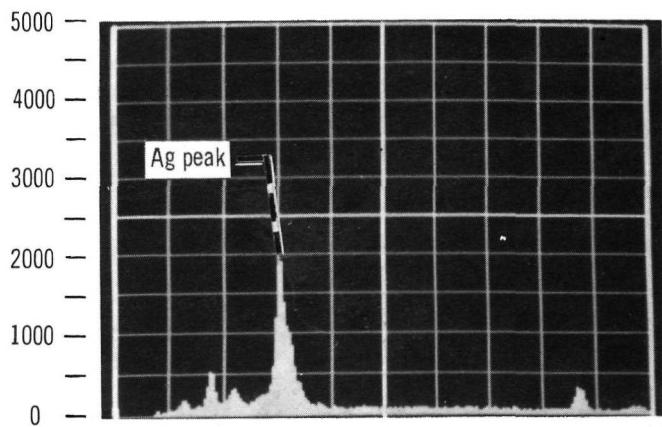
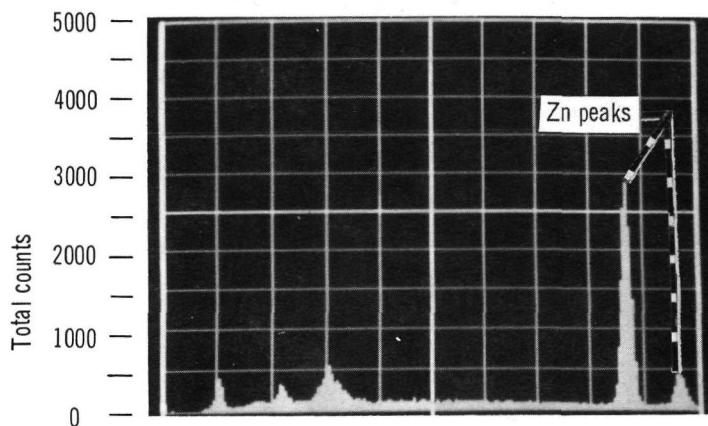


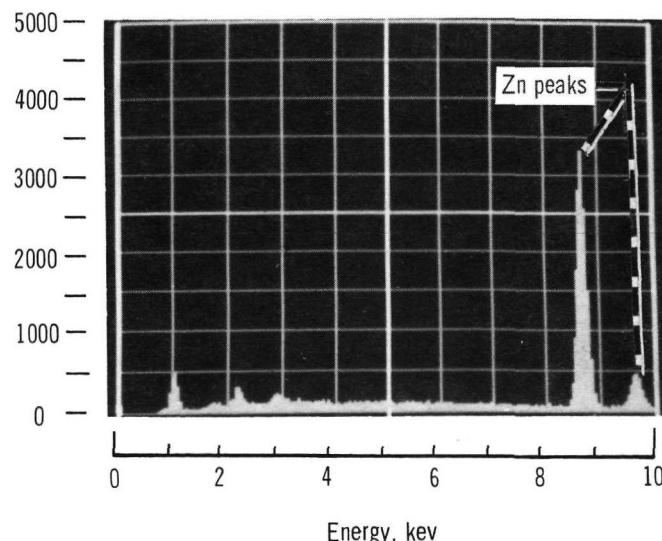
Figure 10. - Schematic diagram of nodule shown in figure 9.



(a) Position 1.



(b) Position 2.



(c) Position 3.

Figure 11. - EDS analysis of areas indicated in figure 9.